Catalytic Cracking of a Gas Oil
Derived from Eastern Canadian Oil Shale

S. H. Ng

Synthetic Fuels Research Laboratory, CANMET
Energy, Mines and Resources Canada
Ottawa, Ontario, Canada K1A 0G1

Introduction

Large oil shale deposits have been discovered in Central and Eastern
Canada.[1] In the past few years, considerable research was conducted on Eastern
oil shales.[2-5] Primary liquid products from retorting of oil shales are superior
to Canadian heavy oil and tar sand bitumen.[5] In a continuing effort to evaluate
the processability of the shale oil produced, a catalytic cracking study on its
gas oil fraction was recently undertaken at CANMET. This paper reports the
primary results.

Experimental Section

The raw shale oil was produced by retorting a New Brunswick oil shale
from Albert Mines near Moncton, New Brunswick. The retort system in the pilot
plant has been reported previously.[5] The shale oil was distilled under vacuum to
give the gas oil fraction which constituted 80 wt % of the feed. For comparison,
a conventional gas oil was obtained from a refinery which processes the Alberta
crudes transported to Eastern Canada through the Interprovincial Pipe Line
(IPPL). The two gas oils were analyzed using ASTM or other accepted methods.
The results are shown in Tables I and II.

Three equilibrium catalysts DA-440, Nova D and GX-30 obtained from
Davison of W. R. Grace were used in this study. Prior to their characterization
and testing, the catalysts were decoked at 590 °C for 3 h. Surface
characteristics were determined by both N_2 adsorption-desorption technique and by
mercury porosimetry. Zeolite surface areas and zeolite contents were estimated
based on a method reported in the literature.[6] Their physical and chemical
properties are given in Table III.

Catalytic cracking of the gas oils was performed in a microactivity
test (MAT) unit which was modified from the ASTM D3907 version. It consists of a
fixed bed quartz reactor packed with 4.2 g of catalyst heated at 470-530 °C in a
three-zone furnace. Feeds were delivered using a syringe pump with catalyst/oil
ratio varying from 2-6 while keeping the hourly weight space velocity (WHSV)
constant at 20 h^{-1}. A flow of nitrogen purge gas at 20 mL/min was maintained
throughout the 20-min test period. Liquid products were collected in a glass
receiver cooled in an ice-water bath whereas the gaseous products were trapped
using water displacement. After the test, both products were quantitatively
measured before analysis. The amount of coke formed on the spent catalyst was
also determined. Conversion was calculated based on the fraction of liquid
product having a boiling point above 216 °C.

Denitrogenation of the shale vacuum gas oil (VGO) was done by both extraction in which dimethylsulfoxide (DMSO) containing 6 wt % 2N sulphuric acid was used as solvent, and adsorption in which an Attapulgus clay was used as adsorbent.

Results and Discussion

Table I shows that the quality of the shale VGO is better than or equivalent to that of the IPPL gas oil except its nitrogen contents are much higher. The basic nitrogen is undesirable in FCC feedstocks as it can neutralize the acid sites of the cracking catalysts resulting in a rapid loss of activity.[7-9] The high nitrogen level is also reflected by the polars in the hydrocarbon type analysis (Table II). Polars in the shale oil may also include oxygen compounds. If these polars are considered crackable, the conversion constraints based on the compositional analysis can be estimated at 80.6 and 81.1 wt % for IPPL and shale VGO respectively, assuming that the diaromatics and the more highly condensed structures including aromatic sulphurs cannot be converted to light products with boiling points less than 216 °C due to the stability of the benzene rings.

Figure 1 shows the effects of temperature and catalyst/oil ratio (C/O) on conversion. Significant differences can be seen between the two feedstocks. For IPPL gas oil, the conversion tends to level off and approaches its limit at high severity. Furthermore, it is less sensitive to the temperature change. On the other hand, for shale VGO, the conversion increases sharply and linearly with C/O ratio and is far below its expected limit even at much higher severity. The conversion is obviously very temperature-dependent. This suggests that the catalysts were seriously poisoned during cracking by the basic nitrogen of shale VGO as this type of poisoning is mainly a surface adsorption phenomenon and high temperature tends to promote desorption. Between the two catalysts, Nova D is apparently more active in cracking IPPL conventional gas oil due to its higher zeolite content. This agrees with Davison's microactivity results (Table III). However, this trend is reversed for shale VGO, with DA-440 being more active. This suggests that the shale oil contains larger molecules which do not have access to the small pores of the zeolite but can be cracked by the matrix of DA-440 which has a larger pore diameter (Table III). A similar phenomenon was also observed in a separate cracking study which deals with other nonconventional gas oils including those derived from resids, tar sand bitumens and heavy oils.[10]

For IPPL gas oil, favourable and optimum gasoline yield (54 wt %) is obtained at about 73% conversion beyond which overcracking seems to take place. The gasoline yield decreases slightly with increased temperature at constant conversion. Between the two catalysts, DA-440 is slightly more selective for gasoline production. This does not necessarily mean that it produces a better gasoline, in terms of higher octane number, as DA-440 is not an octane-enhancing catalyst but Nova D is. It is known that the dealuminated ultra-stable Y zeolite catalysts (USY) yield higher octane gasoline by producing more olefinic compounds,[11] compared with the rare earth exchanged Y zeolite catalysts (REY). For shale VGO, the gasoline yield increases linearly and monotonously with conversion without obvious effects of temperature and catalyst. The experimental maximum gasoline yield is less than 30 wt % which is unacceptably low.

The coke yields of the two gas oils increase exponentially (IPPL) or linearly (shale oil) with conversion. At constant conversion, higher temperature

for the same catalyst tends to lower the coke yield because C/O ratio can be reduced to achieve the same conversion. Contrary to the literature,[11] Nova D (USY) yields more coke than its counterpart DA-440 (REY) in cracking shale VGO whereas for IPPL gas oil, Nova D shows slightly better or equivalent coke selectivity than DA-440. A similar phenomenon was also observed in a separate cracking study involving other nonconventional feedstocks.[10] It is thus believed that the superiority of USY catalysts over REY catalysts with respect to coke selectivity depends also on the nature of the feedstock.

It has been observed that a linear correlation exists between the second-order conversion (conversion/[100 - conversion]) and the coke yield. The linear relationship is expected based on the equations proposed by Wollaston et al.[12] For IPPL gas oil, the straight lines at different temperatures pass through the origin indicating that all the coke formed results from catalytic cracking and is therefore "catalytic" coke.[13] However, for shale VGO, the straight lines intersect the x-axis at different coke values. These values obtained at 0% conversion represent neither "catalytic" coke nor "contaminant" coke since the nickel and vanadium contents of the catalysts are rather low (Table III). This suggests that they belong to the "additive" coke resulting from the basic nitrogen of the shale gas oil which contains little Conradson carbon - another possible precursor for the "additive" coke.[13] The "additive" coke found is independent of the catalyst type and is estimated at 1.47, 1.25, 1.09 and 0.97 wt % at 470 °C, 490 °C, 510 °C and 530 °C, respectively.

Product distribution for the two feedstocks at 50% conversion is shown in Table IV. It can be seen that the shale VGO produces more gases, less gasoline and much more coke compared with IPPL gas oil. The high decant oil yield (39 wt %) for IPPL VGO may be misleading as the majority of its precursor is crackable at higher severity. At 73% conversion, this value drops to 8 wt % raising the gasoline yield from 35 to 54 wt %.

Three methods have been used to achieve higher conversion of the shale oil. The first is to crack with GX-30, a very active catalyst because of its higher zeolite content. The other methods involve upgrading of gas oils by removing some of the nitrogen compounds using either DMSO/acid extraction or Attapulgus clay adsorption. One disadvantage of the rejection methods is the accompanying loss of the hydrocarbon value. Table V shows the weight recovery and the nitrogen contents of the upgraded feedstocks. It is evident that the clay method is superior to the extraction technique since it removes almost 50% more basic nitrogen for the same recovery. Table VI shows a comparison of cracking yields of raw and treated feedstocks cracked at various conditions while keeping catalyst/oil ratio constant at 6. For the untreated shale oil, although the use of GX-30 results in some improvement over DA-440 in conversion and gasoline yield, the coke yield is unacceptably high. Evidently, DMSO raffinate shows better performance than the raw shale oil whereas the clay treated shale oil is the best due to its lowest basic nitrogen content.

Let us consider two approaches in further evaluation of the data: one involves cracking of the raw shale oil as a whole whereas the other involves the separation of the shale oil into two fractions prior to individual cracking under the same conditions. In the latter case, the recovered fraction contains less nitrogen and is therefore better in quality whereas the rejected fraction is assumed, for simplicity, to be unconvertible either because of its high nitrogen level or a refractory nature. One can calculate their cracking yields on a

"total oil" basis by multiplying the yields, based on the recovered portion, with the weight fraction of recovery. The results are illustrated in Fig. 2. Here, the increases in conversion and gasoline yields of the treated shale oils over those of the untreated ones reflect the net poisoning effect on the catalyst by the basic nitrogen.

Based on the data obtained from nitrogen rejection methods (extraction or adsorption), linear correlation can be established between the cracking results, in terms of conversion and gasoline yield, and the basic nitrogen content (1750-4600 ppm) of MAT feeds. A cracking study was also made on the blends prepared from IPPL and raw shale oil. The data points obtained from this dilution method appear to coincide with those from rejection methods over the same basic nitrogen range. This suggests that the rejected portion of the raw shale oil would have been cracked if the catalyst had not been poisoned by the basic nitrogen in the first place. Also, the basic nitrogen content of the shale oil, rather than its compositional differences from the IPPL gas oil, is the determining factor for the cracking yields. Following the trends created by the dilution method, the shale oil produces a cracking result similar to that of IPPL at the same basic nitrogen level, i.e., 72 vs 73.5 wt % in conversion and 51 vs 53 wt % in gasoline yield at 510 °C and a catalyst/oil ratio of 4.

Acknowledgement

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Table I. Feedstock Inspection Data

Properties	IPPL	Shale
°API	24.2	25.0
Aniline point, °C	93.7	80.0
Conradson carbon, wt %	0.43	0.18
Total nitrogen, ppm	1150	7150
Basic nitrogen, ppm	310	4570
Total sulphur, wt %	0.66	0.52
Viscosity at 40 °C, cSt	65.0	17.3
Simulated distillation, °C		
IBP	305	209
10%	369	290
50%	444	394
90%	538	489
FBP	594	536

Table II. Feedstock Compositional Analysis (wt %)

Hydrocarbon type	IPPL	Shale
Paraffins	23.8	21.8
Monocycloparaffins	14.3	13.5
Condensed cycloparaffins	24.2	13.1
Monoaromatics	13.2	16.9
Diaromatics	9.3	11.4
Polynuclear aromatics	7.9	6.1
Polars	4.3	15.4
Aromatic sulphur	2.2	1.4

Table III. Properties of Cracking Catalysts

Properties	DA-440	Nova D	GX-30
Type	REY	USY	REY
BET surface area, m^2/g	75.0	95.5	107.5
Zeolite surface area, m^2/g	43.7	48.4	66.8
Relative zeolite content, wt %	7.3	8.1	10.8
Pore volume, mL/g	0.245	0.266	0.257
Avg. pore diameter, Å	280	208	355
V, ppm	141	351	538
Ni, ppm	374	114	400
Al_2O_3, wt %	42.1	45.3	33.1
Unit cell dimension, Å	24.42	24.28	24.39
Microactivity (Davison), wt %	70	72	78

Table IV. Comparison of Product Yields at 50% Conversion*

Gas oil	IPPL	Shale
Catalyst	DA-440	DA-440
Reactor temperature, °C	470	530
Total dry gas, wt %	1.0	3.5
$C_3 + C_4$, wt %	8.5	13.0
C_5+ gasoline, wt %	35.0	30.0
Light cycle oil, wt %	14.0	27.0
Decant oil, wt %	39.0	20.5
Coke, wt %	2.6	6.6

* Extrapolated data

Table V. Weight Recovery and Nitrogen Contents of Upgraded Shale Oils

Shale oil	Untreated	DMSO	Clay
Recovery, wt %	100	85.3	86.1
Total nitrogen, ppm	7150	5618	3496
Basic nitrogen, ppm	4570	3007	1745

Table VI. Cracking Yields (wt %) at C/O = 6

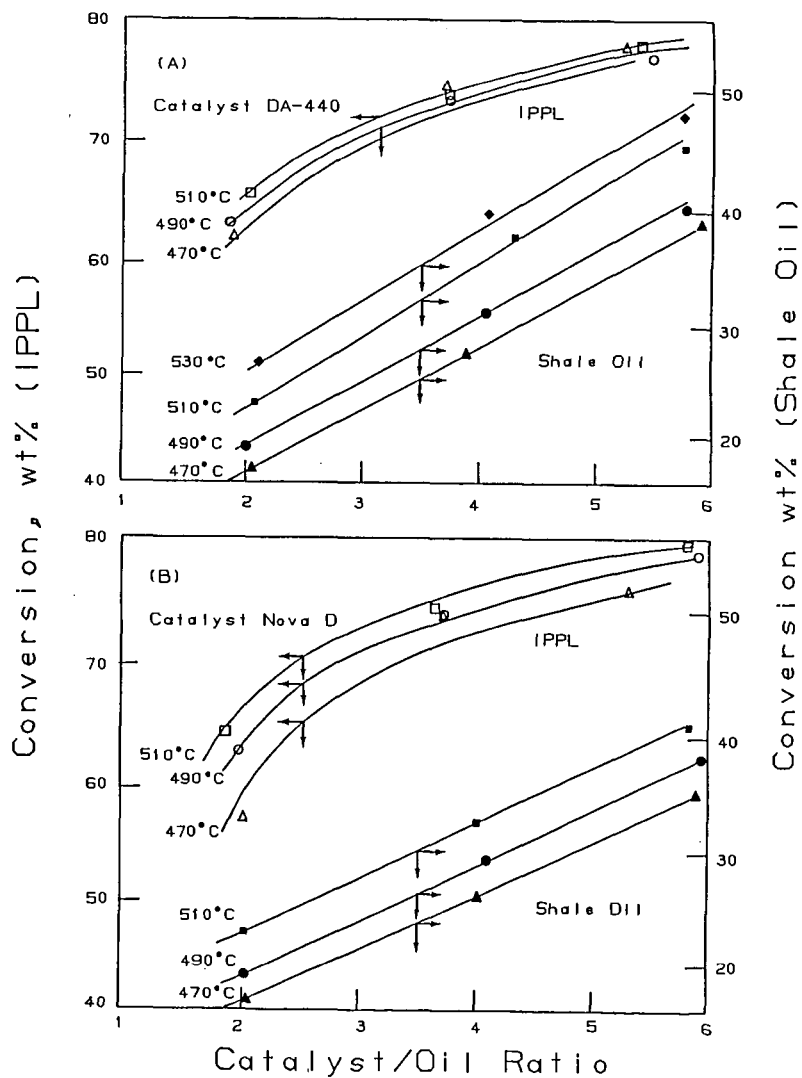| Shale oil	Temp. °C	Catalyst	Conversion	C_5+ Gasoline	Coke
Raw	510	DA-440	45.0	25.2	6.5
DMSO treated	510	DA-440	53.2	31.7	6.4
Clay treated	510	DA-440	65.3	40.0	6.4
Raw	530	DA-440	47.9	26.5	6.6
Raw	530	GX-30	59.8	31.7	9.1
Clay treated	530	DA-440	70.0	42.5	6.4

Figure 1.   Effects of temperature and catalyst/oil ratio
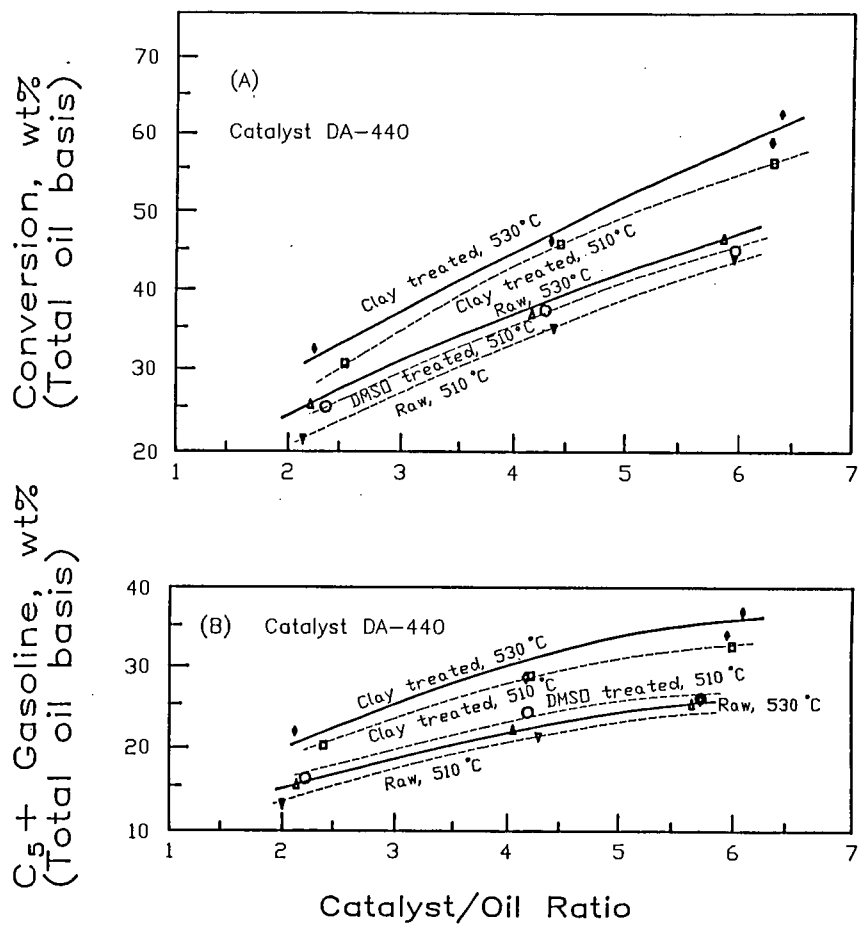on conversion.

Figure 2. Conversions and gasoline yields of raw and treated shale gas oils calculated on total oil basis.